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(54) **GOLDEN ORNAMENT MATERIAL HARDENED BY ALLOYING WITH MINOR COMPONENTS.**

(57) A golden ornament material hardened by alloying pure gold having a purity of 99 % or above with 200-2000 ppm of one or more elements selected from Ca, Be, Ge and B, and, when necessary, 10-500 ppm of one or more elements selected from Mg, Al, Si, Mn, Fe, Co, Ni, Cu, Pd, Ag, In, Sn, Sb, Pb and Bi and/or 10-1000 ppm of one or more rare earth elements including Y based on the total quantity of the resultant mixture.

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TECHNICAL FIELD

Th present invention r lates to gold materials for accessories which are damag d little by rubbing or scratching, as being highly hard to have a Vickers hardness (Hv) of 100 or more, and which maintain said high hardness independently of time or even after heated by brasing or the like.

BACKGROUND ART

Heretofore, in general, Au alloys having an elevated Hv of 100 or more have been popularly used to produce accessories such as neck chains, brooches, rings, etc. Such Au alloys include, for example, K14 alloys and K18 alloys comprising pure gold having a purity of 99 % or more and approximately from 25 to 40 % by weight of alloying components such as Ag, Cu and even Ni, Pd, Zn, etc.

On the other hand, it is said ideal that the above-mentioned accessories are made of pure gold in view of their color and high-quality appearance. However, pure gold has Hv of about 32 as its ingot, while having Hv of about 80 as its worked wire. Even though such pure gold is worked to have an elevated hardness, the elevated hardness of the thus-worked pure gold is inevitably lowered not only with the lapse of time but also when heated by brazing or the like. For these reasons, pure gold accessories are always soft and are therefore easily scratched. It is extremely difficult to keep the esthetic value of such pure gold accessories for a long period of time, and the practical application of pure gold accessories is limited to only an extremely narrow range at present.

DESCRIPTION OF THE INVENTION

We, the present inventors have studied, from the above-mentioned viewpoints, so as to elevate the hardness of pure gold accessories without detracting from their high esthetic value mentioned above and, as a result, have found that;

when pure gold having a purity of 99 % or more is alloyed with from 200 to 2000 ppm, preferably from 800 to 1800 ppm, more preferably from 1000 to 1600 ppm, relative to the total weight of the resulting gold alloy, of one or more alloying components selected from Ca, Be, Ge and B, then the resulting gold alloy can have an elevated Hv of 100 or more, while still maintaining said elevated hardness independently of time or even after heated by brazing or the like, and in addition, since the content of the above-mentioned alloying components is small, the hardened gold alloy can still maintain the color and the high quality of pure gold itself and therefore can be formed into gold accessories capable of maintaining a high esthetic value comparable to that of pure gold accessories for a long period of time, that;

when said pure gold is alloyed with said alloying component(s) and also from 10 to 500 ppm, preferably from 50 to 400 ppm, more preferably from 100 to 300 ppm, relative to the total weight of the resulting gold alloy, of one or more other alloying components selected from Mg, Al, Si, Mn, Fe, Co, Ni, Cu, Pd, Ag, In, Sn, Sb, Pb and Bi, then the resulting gold alloy can have an elevated mechanical strength, and that;

when said pure gold is alloyed with said alloying component(s) and also from 10 to 1000 ppm, preferably from 100 to 500 ppm, more preferably from 200 to 400 ppm, relative to the total weight of the resulting gold alloy, of one or more other alloying components selected from rare earth elements including Y, then the resulting gold alloy can have much more improved plastic workability such as drawing workability and rolling workability.

The present invention has been attained on the basis of the above-mentioned findings and is characterized in that it provides hardened gold materials for accessories comprising;

pure gold having a purity of 99 % or more and from 200 to 2000 ppm, preferably from 800 to 1800 ppm, more preferably from 1000 to 1600 ppm, relative to the total weight of the resulting gold alloy, of one or more alloying components selected from Ca, Be, Ge and B (hereinafter generically referred to as "hardness-improving components"), and optionally,

(a) from 10 to 500 ppm, preferably from 50 to 400 ppm, more preferably from 100 to 300 ppm, relative to the total weight of the resulting gold alloy, of one or more other alloying components selected from Mg, Al, Si, Mn, Fe, Co, Ni, Cu, Pd, Ag, In, Sn, Sb, Pb and Bi (hereinafter generically referred to as "strength-improving components"), and/or

(b) from 10 to 1000 ppm, preferably from 100 to 500 ppm, more preferably from 200 to 400 ppm, relative to the total weight of the resulting gold alloy, of one or more other alloying components selected from rare earth elements including Y (hereinafter referred to as "workability-improving components").

In the present invention, pure gold to be alloyed shall have a purity of 99 % or mor . This is because if gold having a purity of less than 99 % is alloyed according to the present invention, the resulting gold alloy

no more has the golden color which pure gold possesses and therefore loses the high-quality appearance of pur gold.

The reason why the content of th hardness-improving compon nt(s) is defined to fall within the range betw en 200 ppm and 2000 ppm is because, if it is less than 200 ppm, it is impossible to levate the hardness of the resulting gold alloy to have Hv of 100 or more and is also impossible to prevent the thus-elevated hardness of the gold alloy from being lowered with the lapse of time or when the gold alloy is heated. On the other hand, if said content is more than 2000 ppm, the gold alloy can no more have the color and the high-quality appearance of pure gold itself with the result that the esthetic value of the gold alloy is lowered.

The reason why the content of the strength-improving component(s) and that of the workability-improving component(s) are defined to fall within the range between 10 ppm and 500 ppm and within the range between 10 ppm and 1000 ppm, respectively, is because, if they are less than 10 ppm, it is impossible to attain the intended effects to improve the mechanical strength and the plastic workability of the gold alloy. On the other hand, if they are more than 500 ppm or 1000 ppm, the color of the gold alloy is noticeably worsened.

BEST MODES OF PRACTICING THE INVENTION

Next, the gold materials for accessories of the present invention are described concretely by means of their examples.

Pure gold having a purity shown in Tables 1 to 6 was melted in an ordinary vacuum melting furnace, to which was/were added alloying component(s) of the amount(s) also shown in Tables 1 to 6. Next, the resulting gold alloy was cast into a columnar ingot having a diameter of 20 mm and a length of 100 mm, and test pieces were cut out of the ingot. The hardness (micro-Vickers hardness under 100 gr) of the test piece was measured. The test piece was chamfered and then introduced into a single-head drawing machine where it was repeatedly drawn by 20 passes to be formed into a wire having a diameter of 0.5 mm. In this way, gold alloy wire samples, Nos. 1 to 55 of the present invention were prepared. As a control, a pure gold wire sample was prepared in the same manner as above, except that no alloying component was added.

The hardness (micro-Vickers hardness under 100 gr) of each of these wire samples was measured immediately after having been drawn and after having been stored for 6 months. In addition, each wire sample was, immediately after having been drawn, heated at 450 °C for 30 minutes and then cooled under the conditions corresponding to those for ordinary brazing, for example, using a soldering alloy of Au:3 wt.%-Si having a melting point of 370 °C or a soldering alloy of Au:12 wt.%-Ge having a melting point of 350 °C. The hardness of each of the thus heat-treated wire samples was also measured in the same manner as above. In order to evaluate the mechanical strength of each wire sample, the tensile strength of each wire sample was measured immediately after having been drawn. The results obtained are shown in Tables 7 to 10.

Table 1

Samples		Purity of Pure gold (%)	Content(s) of Alloying Component(s) (ppm)		
			Hardness-improving Component(s)	Strength-improving Component(s)	Workability-improving Component(s)
Gold Alloy Wire Samples of the Invention for Accessories	1	99. 69	Ca:404	–	–
	2	99. 84	Be:841	–	–
	3	99. 38	Ge:865	–	–
	4	99. 85	B:391	–	–
	5	99. 56	Ca:573, Be:798	–	–
	6	99. 35	Be:68, Ge:584	–	–
	7	99. 37	Ge:92, B:420	–	–
	8	99. 94	Ca:508, Be:73, Ge:376	–	–
	9	99. 67	Be:876, Ge:599, B:504	–	–
	10	99. 39	Ca:388, Be:430, Ge:18, B:359	–	–

Table 2

Samples		Purity of Pure gold (%)	Content(s) of Alloying Component(s) (ppm)		
			Hardness-improving Component(s)	Strength-improving Component(s)	Workability-improving Component(s)
Gold Alloy Wire Samples of the Invention for Accessories	11	99.61	Ca:481	–	Y:699
	12	99.90	Be:1535	–	La:615
	13	99.86	Ge:231	–	Ce:740
	14	99.45	B:629	–	Pr:810
	15	99.95	Ca:401, Be:157	–	Nd:101
	16	99.64	Be:845, Ge:770	–	Pm:26
	17	99.72	Ge:615, B:774	–	Sm:899
	18	99.87	Ca:298, Ge:335	–	Eu:543
	19	99.52	Be:539, B:1001	–	Gd:921
	20	99.40	Ge:241, B:56	–	Tb:559

Table 3

Samples		Purity of Pure gold (%)	Content(s) of Alloying Component(s) (ppm)		
			Hardness-improving Component(s)	Strength-improving Component(s)	Workability-improving Component(s)
Gold Alloy Wire Samples of the Invention for Accessories	21	99.43	Ca:599, Ge:388, B:27	–	Dy:17
	22	99.75	Be:269	–	Y:727, La:29
	23	99.77	Ge:639	–	La:195, Ce:474
	24	99.43	B:1055	–	Pr:324, Nd:19
	25	99.43	Ca:692	–	Pm:668, Sm:83
	26	99.67	Ca:49, Be:399	–	Eu:682, Gd:49
	27	99.95	Ge:503, B:231	–	Y:219, Tb:283, Dy:111
	28	99.44	Be:469, Ge:33	–	La:84, Pr:578, Pm:327
	29	99.86	Ge:899	–	Eu:224, Gd:198, Tb:253
	30	99.73	Be:579	–	Ce:58, Pr:268, Nd:123, Pm:59

Table 4

Samples		Purity of Pure gold (%)	Content(s) of Alloying Component(s) (ppm)		
			Hardness-improving Component(s)	Strength-improving Component(s)	Workability-improving Component(s)
Gold Alloy Wire Samples of the Invention for Accessories	31	99.34	Ca:776	Mg:225	–
	32	99.54	Be:212	Al:273	–
	33	99.52	Ge:619	Si:197	–
	34	99.46	B:918	Mn:241	–
	35	99.65	Ca:582, Be:18	Fe:66	–
	36	99.37	Ge:180, B:360	Co:91	–
	37	99.83	Ca:199, Be:203, Ge:15	Ni:247	–
	38	99.46	Ca:84, Be:51, Ge:910, B:483	Cu:220	–
	39	99.57	Ca:934	Pd:196	Y:102
	40	99.92	Be:890	Ag:62	Ce:620

Table 5

Samples		Purity of Pure gold (%)	Content(s) of Alloying Component(s) (ppm)		
			Hardness-improving Component(s)	Strength-improving Component(s)	Workability-improving Component(s)
Gold Alloy Wire Samples of the Invention for Accessories	41	99. 97	Ge:704	In:181	Nd:989
	42	99. 44	B:959	Sn:308	Sm:237
	43	99. 83	Ca:876, Ge:890	Sb:148	Gd:731
	44	99. 87	Be:513, B:895	Pb:97	Dy:402
	45	99. 91	Be:157, Ge:608	Bi:231	Y:389, Ce:520
	46	99. 85	Ca:527	Mg:237, Al:121	Pr:394
	47	99. 84	Be:584	Si:253, Mn:11	Nd:587, Sm:105
	48	99. 90	Ge:1289	Fe:47, Co:284	Pr:432, Pm:210, Gd:13

Table 6

Samples		Purity of Pure gold (%)	Content(s) of Alloying Component(s) (ppm)		
			Hardness-improving Component(s)	Strength-improving Component(s)	Workability-improving Component(s)
Gold Alloy Wire Samples of the Invention for Accessories	49	99.91	B:489	Ni:67, Cu:181	La:56, Nd:99, Eu:123, Tb:59
	50	99.86	Ca:235, B:52	Pd:29, Ag:144, In:69	Ce:144, Pm:6, Gd:19
	51	99.58	Ca:452, Ge:326	Sn:222, Sb:117, Pb:26	Pr:45, Eu:399
	52	99.91	Be:669, B:268	Co:188, Ag:59, Bi:263	Nd:33
	53	99.53	Ca:456, Ge:364	Al:165, Mn:26, Co:79, Cu:110	Ce:59, Sm:628
	54	99.40	Be:1698	Ni:120, Pd:33, In:56, Sn:139	Dy:23
	55	99.72	Ca:523, Ge:698	Mg:87, Si:59, Fe:129, Cu:44, Ag:168	Ce:19
Pure Gold Wire Sample for Accessories		99.99	-	-	-

Table 7

Samples		Hardness (H v)				Tensile Strength (kg/mm^2)
		Ingot	Immediately After Being Drawn	After Being Stored for 6 Months	Immediately After Being Heated	
Gold Alloy Wire Samples of the Invention for Accessories	1	53	105	104	104	37. 7
	2	59	110	110	109	41. 9
	3	57	109	108	107	39. 2
	4	51	104	104	104	37. 8
	5	62	119	119	118	41. 8
	6	61	117	117	116	40. 8
	7	58	109	109	109	40. 0
	8	63	121	120	120	42. 6
	9	56	123	123	119	47. 7
	10	63	121	121	119	45. 8
	11	69	137	137	136	46. 2
	12	73	141	141	138	48. 9
	13	68	128	128	126	47. 1
	14	62	120	120	117	42. 9

Table 8

Samples		Hardness (H v)				Tensile Strength (kg/mm²)
		Ingot	Immediately After Being Drawn	After Being Stored for 6 Months	Immediately After Being Heated	
Gold Alloy Wire Samples of the Invention for Accessories	15	57	113	113	112	41. 7
	16	64	128	128	125	48. 8
	17	72	141	141	138	49. 9
	18	66	124	124	122	48. 6
	19	71	143	143	142	51. 2
	20	57	115	115	113	44. 3
	21	65	131	131	128	43. 8
	22	65	132	132	127	46. 7
	23	58	114	114	112	44. 8
	24	62	123	122	123	49. 0
	25	55	111	111	111	42. 5
	26	59	119	119	115	45. 8
	27	63	123	123	122	46. 8
	28	68	131	131	128	49. 3

Table 9

Samples		Hardness (Hv) Ingot	Immediately After Being Drawn	After Being Stored for 6 Months	Immediately After Being Heated	Tensile Strength (kg/mm^2)
Gold Alloy Wire Samples of the Invention for Accessories	29	65	130	130	130	50.3
	30	53	125	125	123	47.6
	31	65	126	126	124	52.3
	32	67	135	135	134	54.8
	33	59	112	112	110	53.5
	34	59	118	118	115	53.2
	35	62	121	121	120	53.8
	36	66	131	131	129	53.1
	37	59	119	119	118	52.8
	38	56	131	132	128	55.8
	39	64	129	129	127	55.7
	40	66	131	131	127	55.4
	41	62	129	129	127	61.3
	42	60	121	121	119	56.8

Table 10

Samples		Hardness (Hv)				Tensile Strength (kg/mm²)
		Ingot	Immediately After Being Drawn	After Being Stored for 6 Months	Immediately After Being Heated	
Gold Alloy Wire Samples of the Invention for Accessories	43	75	143	143	143	62.5
	44	68	139	139	137	58.3
	45	61	126	126	124	52.7
	46	66	129	129	127	53.8
	47	63	130	130	128	55.6
	48	72	140	140	138	56.9
	49	59	123	123	121	54.8
	50	61	123	123	120	58.8
	51	64	131	131	130	59.3
	52	61	124	124	123	60.1
	53	63	127	127	125	57.7
	54	75	142	142	142	62.3
	55	62	127	127	127	60.4
Pure Gold Wire Sample for Accessories		32	80	35	30	31.6

From the results shown in Tables 1 to 10, it is known that all the gold alloy wire samples of the present invention, Nos. 1 to 55 always had a high hardness, namely, Hv of 100 or more even after being stored or even after being heated, while the hardness of the pure gold wire sample having Hv of less than 100 was noticeably lowered after being stored and after being heated. It is therefore obvious that the stability of the hardness of the gold alloy wire samples of the present invention is significantly higher than that of the pure gold wire sample and that the mechanical strength of the former containing strength-improving component-

(s) was extremely improved.

As m ntioned hereinabov , th gold materials for accessories of th present invention are hardly scratched as stably and always having an elevated Hv of 100 or mor even after being stored or heated. Moreover, since the content of the alloying components in the gold materials of the present invention is small, the gold materials have, in addition to said high hardness, an esthetic value comparable to the excellent esthetic value of pure gold and maintain said esthetic value for a long period of time due to their high hardness. The gold materials for accessories of the present invention thus have practically useful characteristics.

Claims

1. A hardened gold material for accessories comprising;
   pure gold having a purity of 99 % or more and from 200 to 2000 ppm, relative to the total weight of the resulting gold alloy, of one or more alloying components selected from Ca, Be, Ge and B.

2. A hardened gold material for accessories comprising;
   pure gold having a purity of 99 % or more, from 200 to 2000 ppm, relative to the total weight of the resulting gold alloy, of one or more alloying components selected from Ca, Be, Ge and B, and from 10 to 500 ppm, relative to the same, of one or more other alloying components selected from Mg, Al, Si, Mn, Fe, Co, Ni, Cu, Pd, Ag, In, Sn, Sb, Pb and Bi.

3. A hardened gold material for accessories comprising;
   pure gold having a purity of 99 % or more, from 200 to 2000 ppm, relative to the total weight of the resulting gold alloy, of one or more alloying components selected from Ca, Be, Ge and B, and from 10 to 1000 ppm, relative to the same, of one or more other alloying components selected from rare earth elements including Y.

4. A hardened gold material for accessories comprising;
   pure gold having a purity of 99 % or more, from 200 to 2000 ppm, relative to the total weight of the resulting gold alloy, of one or more alloying components selected from Ca, Be, Ge and B, from 10 to 500 ppm, relative to the same, of one or more other alloying components selected from Mg, Al, Si, Mn, Fe, Co, Ni, Cu, Pd, Ag, In, Sn, Sb, Pb and Bi, and from 10 to 1000 ppm, relative to the same, of one or more other alloying components selected from rare earth elements including Y.

INTERNATIONAL SEARCH REPORT

International application No. PCT/JP94/00920

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl^5 C22C5/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl^5 C22C5/00-5/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, A, 62-290836 (Tanaka Denshi Kogyo K.K.), December 17, 1987 (17. 12. 87), Lines 5 to 8, left column, page 1 and lines 7 to 8, upper right column, page 2, (Family: none)	1
X	JP, A, 2-170931 (Mitsubishi Metal Corp.), July 2, 1990 (02. 07. 90), Lines 5 to 16, left column, page 1, (Family: none)	1-4
X	JP, A, 1-87734 (Tanaka Kinzoku Kogyo K.K.), March 31, 1989 (31. 03. 89), Lines 5 to 8, left column, page 1 and lines 6 to 11, lower right column 1, page 2, (Family: none)	1-4
P	JP, A, 6-179931 (Mitsubishi Materials Corp.), June 28, 1994 (28. 06. 94), Lines 2 to 7, left column, page 2, (Family: none)	2

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search August 30, 1994 (30. 08. 94)	Date of mailing of the international search report September 13, 1994 (13. 09. 94)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP94/00920

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, A, 58-16041 (Mitsubishi Metal Corp.), January 29, 1983 (29. 01. 83), Line 5, left column to line 19, right column, page 1 & GB, A, 2,102,768	1-4